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CHEMICAL AND PHYSICAL METHODS FOR THE CONTROL OF SAPONIFIED CRESOL SOLUTIONS

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CONTENTS

	Page		Page
Purpose of discussion	1	Fractional distillation of the total phenols	20
Fundamental requirements for saponified cresol solutions	2	Tentative standards and results of the examination of some commercial samples	21
Physical tests	5	Summary	23
Estimation of total fixed alkali	6	Literature cited	24
Estimation of excess fixed alkali	6		
Estimation of total phenols	8		
Estimation of benzophenol	17		

PURPOSE OF DISCUSSION

UNDER regulations promulgated by the Secretary of Agriculture, at present embodied in B. A. I. Order 273 (*6*)[1], the Bureau of Animal Industry is charged with the disinfection of premises and vehicles which may have become infected by diseased animals in course of interstate transportation, as well as with the disinfection of the animals themselves under certain conditions. Inasmuch as the bureau is held responsible for the results of disinfection, it must necessarily possess the power to prescribe the means by which the results shall be attained, including the chemical composition and the physical properties of the disinfectants to be used.

This bulletin discusses "saponified cresol solutions" as official disinfectants but does not undertake exhaustively to cover products intended for other applications or subject to other criteria. The Bureau of Animal Industry began to depart from the requirements of the Pharmacopœia for liquor cresolis compositus in 1915, successively permitting the use of a cheaper grade of commercial cresol, a smaller proportion of linseed oil, sodium hydroxide instead of potassium hydroxide, and finally soybean oil or its fatty acids in lieu of linseed oil. These changes, some of which were followed in the ninth revision of the Pharmacopœia, were obviously for the purpose of economy. Other departures from the pharmacopœial speci-

[1] Figures in italic in parentheses refer to literature cited, p. 24.

fications, such as a requirement for a minimum content of total phenols by analysis and a restriction on excess alkali, were aimed either to insure uniform effectiveness or to reduce the chance of injury to animals.

The standard procedure for the chemical examination of saponified cresol solutions has been one developed by the writer (*1*). Its chief merit has lain in the circumstance that different analysts could obtain results in good agreement, so that wherever it has been consistently employed by manufacturers, consumers, and regulatory officials there has been little room for dispute over the analytical data pertaining to a given sample. But because it is cumbersome and tedious it is not well adapted to afford the ready control desirable for such products, particularly in the plant laboratory. The purpose of the present paper is to present a procedure which is rapid and simple enough for the plant laboratory and sufficiently precise and accurate for use by the regulatory official. At present this procedure is limited to saponified cresol solutions, composed essentially of cresol and soap, and has not been extended to coal-tar-creosote dips and disinfectants.

FUNDAMENTAL REQUIREMENTS FOR SAPONIFIED CRESOL SOLUTIONS

In order to devise an appropriate procedure for testing a commercial preparation designed for a specific use, it is first necessary to understand the exact functions which the preparation is called upon to perform and the range of external conditions under which it must successfully perform them. In the work of the Bureau of Animal Industry the functions of a saponified cresol solution are (1) to make inactive the germs of certain diseases, (2) to devitalize certain insects which cause disease either directly or by acting as intermediate hosts for disease-producing organisms, and (3) to destroy the vitality of the eggs of such insects. To accomplish these results it is sometimes necessary to disinfect the whole surface of the animals themselves by dipping or spraying, in which case the preparation must not cause injury to the animals. Under practical conditions of use it is frequently impossible to protect the concentrated preparation against long exposure to a low temperature during transportation and storage. Again, before it can be used it must be dissolved in water, and frequently this means that the solution must be prepared in rather large quantities with cold water, which may also be hard water, by men not especially versed in such manipulations, working with scanty equipment in physical discomfort and pressed for time.

Given the exact functions and the conditions under which the preparation must perform these functions, the next step is to formulate an appropriate set of specifications. In the present discussion it is proper to suggest only the general form which such specifications may take, leaving precise details and limits to be promulgated by the bureau in the form of regulatory orders.

UNIFORMITY AT LOW TEMPERATURES

A saponified cresol solution normally becomes more viscous when chilled and may even set to a jelly which can not be poured from the container. Material in such a condition might be highly inconvenient

for use in the field and consequently the congealing point should lie below an appropriately chosen temperature. Instead of forming a uniform jelly with the cresol, the soap sometimes tends to separate in isolated particles which first render the solution turbid and later rise to the surface, where they become agglomerated into a mass of separated soap. Such a condition is objectionable, because the uniformity of the preparation is lost and is not readily recovered again in commercial containers handled under field conditions after the temperature has risen. The necessity for avoiding separation at low temperatures will operate to restrict the manufacturer with respect to both the maximum percentage of soap in his product and the nature of the fatty acids constituting the soap; possibly, too, with respect to the nature of the alkali.

SUFFICIENTLY RAPID RATE OF SOLUTION

Varying primarily with the proportion of soap and its nature, there is a considerable tendency for a saponified cresol solution to lose its original fluidity when added to water and to form masses or particles of jelly. Such a material may be completely soluble, but may dissolve so slowly, especially in cold water, that it becomes objectionable in the field. The presence of jelly particles may easily escape the notice of the operator, and the application of such a suspension in place of a uniform solution might conceivably cause serious injury to animals, particularly to their eyes, and in general could not be trusted to exert uniformly reliable germicidal or insecticidal effects. The necessity for a sufficiently rapid rate of solution has been the chief reason why the soaps of so few fats or oils have been considered appropriate for use in making saponified cresol solutions.

SOLUBILITY

A saponified cresol solution should form a practically clear solution with distilled water. A few particles of solid matter are probably of no significance, but there should be no globules present, however minute. Such globules may consist of highly concentrated cresol and are objectionable for much the same reasons as apply to masses of undissolved jelly. Their presence may be due (1) to the use of an impure cresol which contains a considerable proportion of hydrocarbons, (2) to a high proportion of high-boiling phenolic homologues in the commercial cresol, (3) to a high percentage of total phenols, (4) to unsaponified fatty oil or fatty acids, or (5) to a low proportion of soap. A requirement for the absence of globules on dilution therefore automatically restricts the manufacturer in all these particulars.

THE PERCENTAGE OF NEUTRAL SOAP

Although the germicidal and insecticidal efficiency of cresol is very likely modified by admixture with various proportions of various kinds of soaps, it must be presumed that the only real reason for the presence of soap is to render the cresol more soluble. Certainly the addition of soap is never recommended for solutions of benzophenol, a homologue already sufficiently soluble. As noted, specifications relative to resistance to low temperature, and to rate

and degree of solubility, will go far toward restricting the proportion and the nature of the soap which may be present in a saponified cresol solution. So long as these specifications are met it appears scarcely necessary to inquire further, as a matter of routine, into the nature of the fatty acids which may be present in a given sample or even to set a maximum limit on the percentage of soap, but undoubtedly it is necessary to set a minimum limit. A certain margin of soap above the proportion barely necessary to bring the cresol into solution is desirable in order to provide for unforeseen vicissitudes, such as the use of hard water. Inasmuch as the nature of the fatty acids, which vary in molecular weight, appears not to demand determination, the control of the neutral soap present may be most fairly, as well as most conveniently, made by controlling the percentage of alkali which is combined in the form of soap.

RESTRICTION OF EXCESS ALKALI

In addition to alkali combined as soap, an excess may be present owing either to faulty following of a formula or to incomplete saponification of glycerides. A slight excess is justifiable and perhaps even desirable, but above a certain proportion it becomes objectionable because it may render the final solution unnecessarily severe upon animals. Accordingly the excess alkali should be restricted by a maximum limit.

PERCENTAGE LIMITS OF TOTAL PHENOLS

The important active ingredient in saponified cresol solutions is the "total phenols," comprising all homologues present. In addition to a minimum percentage limit which obviously must be set, a maximum limit is also desirable because animals may be poisoned by treatment with too strong phenolic solutions.

PERCENTAGE LIMIT OF BENZOPHENOL

Commercial cresol always contains benzophenol (C_6H_5OH), sometimes in large proportion. Not only is benzophenol a much weaker germicide than cresol, but it is also more rapidly absorbed by the tissues of the higher animals and is consequently more dangerously poisonous. For both reasons it appears necessary to set a maximum limit to the proportion of benzophenol which may be present in a saponified cresol solution.

PROPORTION OF HIGH-BOILING PHENOLIC HOMOLOGUES

Inasmuch as the formation of globules upon dilution becomes increasingly more likely to occur as the boiling point of the mixture of phenolic homologues rises, it is justifiable to set an upper limit to the distillation range of the commercial cresol that may be employed in compounding a saponified cresol solution.

On the basis of the preceding discussion, the following skeleton specifications are suggested as fundamental and essential:

(*a*) The product shall remain a uniform liquid when held at a temperature of _____ for _____ hours.

(*b*) It shall dissolve completely in 30 parts water at a temperature of _____ within _____ minutes, affording a solution entirely free from globules, and not more than faintly opalescent.

(*c*) It shall contain soap, exclusive of excess alkali, equivalent to not less than _____ per cent of sodium hydroxide, and the excess alkali shall be equivalent to not more than _____ per cent of sodium hydroxide.

(*d*) It shall contain not less than _____ per cent and not more than _____ per cent total phenols, not more than _____ per cent of benzophenol, and not more than _____ per cent of phenols distilling above a temperature of _____.

It will now be in order to formulate methods of test whereby the analyst may determine whether a given sample meets the specifications.

PHYSICAL TESTS

The probable performance of complex materials in service may often be judged better by a few well-chosen physical tests than by data from a chemical analysis. An ideal physical test would subject the sample to an exact replica of service conditions; but in practice it is usually necessary to adhere strictly to a set of more or less arbitrary conditions which imitate possible service conditions only partially and imperfectly.

THE CHILL TEST

A test tube, approximately 180 by 20 millimeters, is half filled with the sample, stoppered, and immersed at least three-fourths in a bath held at the desired temperature for the desired period. The contents of the tube immediately after withdrawal from the bath should flow when the tube is tilted and should show no separation of soap, either in mass or as a pronounced turbidity.

THE SOLUTION-RATE TEST

An ordinary 250 cubic centimeter glass-stoppered graduated cylinder about 35 centimeters in height and holding about 300 cubic centimeters to the neck, is filled nearly to the neck with distilled water at the desired temperature and a single ordinary "marble" measuring 12 to 14 millimeters in diameter is dropped in. Ten cubic centimeters of the sample, free from froth, is rapidly poured from a graduate into the cylinder without touching its walls. The cylinder is quickly filled to overflowing with more distilled water at the same temperature and the stopper is inserted without entrapping any air; then the cylinder is held vertically between the hands and inverted sharply once every 2.5 seconds—that is, brought through a complete cycle of positions in each 5 seconds. At the expiration of a fixed time counting from the first contact, the result should be a practically clear solution in which no jelly particles or globules of the undissolved sample are present. The test is valid only when the first inversion is made before any of the sample has fallen to the bottom of the cylinder and formed a layer thereon.

THE SOLUBILITY-DEGREE TEST

If the solution obtained in the solution-rate test is perfectly transparent and clear, the degree of solubility is satisfactory. Otherwise the solution is poured into a capacious flask, swirled a short time to insure solution of jelly particles, and then examined for globules, first with a hand magnifying glass, and finally, if neces-

sary, in an appropriate cell under a compound microscope. Occasional particles of solid matter are of no significance, but globules should be entirely absent. It must be remembered that this test is made with distilled water, so that even if very few and very minute globules appear it may be presumed that the product will suffer pronounced breaking when mixed with the harder waters employed in the field.

THE ESTIMATION OF TOTAL FIXED ALKALI

The method here recommended is based upon one in common use for determining the total alkali in hard soaps, whereby a hot aqueous solution of the sample is treated with standard mineral acid in excess, the solidified cake of fatty acids removed after cooling, and the excess acid titrated back with standard alkali and an appropriate indicator, such as methyl orange. Two additional steps are needed to make the method applicable to saponified cresol solutions—tar bases must be first expelled by evaporation, inasmuch as they are alkaline toward methyl orange, and stearic acid must be added in order to stiffen the separated fatty acids and cresol sufficiently to form a cake.

Approximately 10 grams of the sample are weighed by difference into a 200 cubic centimeter beaker and reduced nearly one-half, or until no odor of tar bases is perceptible, by evaporation on a steam bath or on a hot plate, provided the temperature is maintained low enough to avoid decomposition which would produce a discolored solution for final titration. The residue is dissolved on the steam bath in about 100 cubic centimeters of water, then half-normal mineral acid is run in from a burette until a drop of the well-stirred liquid produces a deep blue spot upon Congo red test paper. About 5 grams of stearic acid is added and the beaker is heated upon the steam bath until the stearic acid is entirely melted, when the whole is vigorously stirred, left about 15 minutes for the layers to separate, and then cooled until the fatty acids form a firm cake. After filtration, during which the filtrate is repassed if necessary to obtain perfect clarity, and washing with cold water, the filtrate is titrated with half-normal alkali and with methyl orange as indicator. From the net consumption of standard acid is calculated the percentage of total alkali in the sample, expressed as sodium hydroxide. The stearic acid used must be neutral as respects methyl orange, but need not otherwise be of highest purity.

THE ESTIMATION OF EXCESS FIXED ALKALI

The excess alkali in ordinary soaps is commonly determined (*7*) through the titration of an alcoholic solution with phenolphthalein as indicator. That method can not be applied directly to saponified cresol solutions, because cresols in alcoholic solution react decidedly acid toward phenolphthalein. But if Poirrier blue C 4 B (*3*) be employed as indicator and the end point be observed in a special manner, the titration affords sufficiently accurate results. When soap only is present the color of the indicator undergoes a sharp change from cherry to blue, with sometimes a violet intermediate stage, at the same point at which phenolphthalein is changed from rose to

colorless. But when cresol also is present, the final change is only from violet to blue and is too indistinct for observation in the titration flask. Moreover, the colors fade rather rapidly in the presence of cresol. These difficulties led to the adoption of the following method:

About 10 grams of the sample are weighed by difference into a 200 cubic centimeter Erlenmeyer flask and dissolved in 100 cubic centimeters of 95 per cent alcohol previously rendered neutral to either phenolphthalein or Poirrier blue. A supply of clean and dry test tubes or vials is provided, measuring about 60 by 12 millimeters, also a 0.5 per cent alcoholic solution of Poirrier blue C 4 B and a 3 per cent aqueous solution of acetic acid, with droppers for each. Between 0.5 and 1 cubic centimeter of the alcoholic solution of the sample is poured into one of the test tubes and mixed with sufficient indicator drop by drop, to produce a pronounced color; then, with the tube held against the light, 1 drop of the dilute acetic acid is added and a change in color is looked for. If no change occurs, the sample contains no excess alkali. If treatment with acetic acid effects a change toward blue, half-normal acid is run into the flask from a burette, in quantity depending upon the effect produced by acetic acid in the test, but not restricted by fear of somewhat overrunning the end point. After mixing, 1 cubic centimeter is tested as before. The end point is reached when a drop of the acetic acid leaves the color of the test unchanged; that is, it is approached from the alkaline side, but if overrun, the solution may be brought back to alkaline reaction with half-normal alkali from a burette and once more titrated with acid. From the net consumption of standard acid is calculated the percentage of excess alkali, expressed as sodium hydroxide. Tar bases do not react alkaline toward the indicator.

It will be evident that contamination of the throat of the flask by drops of the standard acid or alkali must be avoided, else such might be washed into the test tube and vitiate the test. A clean, dry tube should be used for each test, and the contents should be immediately discarded after the test, not returned to the flask or held for later observation. The blue given by a strictly neutral solution may become more intense through copious addition of acid, particularly of a highly ionized acid. Accordingly a 15 per cent alcoholic solution of oleic acid may be preferable to the 3 per cent aqueous solution of acetic acid, but the latter is entirely satisfactory if only 1 drop is used.

EXPERIMENT 1

Oleic acid, 2 cubic centimeters, was dissolved in 100 cubic centimeters of 95 per cent alcohol, phenolphthalein was added, then 10 per cent aqueous sodium hydroxide in excess, and finally half-normal hydrochloric acid until 1 drop discharged the pink color. After the addition of 5 cubic centimeters of redistilled commercial cresol 1 cubic centimeter of the solution appeared to be acid when tested with Poirrier blue. Accordingly 0.5 cubic centimeter of half-normal sodium hydroxide was added, and then the solution gave a reddish violet test which underwent a very pronounced change to blue upon the addition of 1 drop of 5 per cent acetic acid. Titration from that point with half-normal hydrochloric acid then produced the following effect: After 0.2 cubic centimeter, a dull violet, very much modi-

fied by 1 drop of acetic acid; after 0.3 cubic centimeter, a dull blue, much brightened by acetic acid; after 0.4 cubic centimeter, a similar but considerably less pronounced effect; after 0.5 cubic centimeter, a clear blue, apparently brightened a little by acetic acid; after 0.6 cubic centimeter, a clear blue, not apparently affected by 1 drop of 5 per cent acetic acid.

The percentage of alkali combined as soap will be the difference, expressed as sodium hydroxide, between the percentages of total and of excess fixed alkali.

THE ESTIMATION OF TOTAL PHENOLS

The determination of the percentage of total phenols in a saponified cresol solution is at once the most important and the most troublesome of the necessary examinations. The former method (*1*) of the writer was specifically stated to be accurate only when applied to certain phenols, or to a balanced mixture of phenols which constitutes what might be provisionally termed a "normal" commercial cresol. As the composition of the sample in hand departs from the "normal," so the analytical results depart from accuracy, being too low for low-boiling mixtures and too high for high-boiling mixtures, while such phenols as are difficultly volatile with steam tend to escape recovery. So long as the method was used in the analysis of both a commercial cresol and the saponified cresol solution prepared therefrom, these discrepancies were neither very apparent nor of serious practical importance. But at present the method of Weiss (*8*) is largely used for analyzing commercial cresols; and inasmuch as results thereby obtained are not similarly affected by the boiling range of the sample, it is possible for the two methods to disagree seriously. Others (*4*) (*5*) have not failed to emphasize this situation but have offered no remedy or alternative.

Inasmuch as the method of Weiss has received wide acceptance for the analysis of commercial cresol, it will be logical to extend it to saponified cresol solutions, if possible. The most recent description of the Weiss method for "tar acids" is given by Hill (*5*) under the auspices of the same manufacturing firm that sponsored the work of Weiss. Preliminary to the application of the method to saponified cresol solutions it has been necessary to submit its possible sources of error to a more searching examination than has yet appeared in the literature. Hill prescribes that 25 cubic centimeters of the sample of cresol shall be diluted with 75 cubic centimeters of purified kerosene and the mixture distilled to decomposition. The distillate is received in a graduated separatory funnel of special type, freed from water, measured, thoroughly extracted with a solution of sodium hydroxide, and again measured. The decrease in volume of the distillate is assumed to represent an equal volume of "tar acids."

Two samples of commercial cresol were employed in the experiments hereinafter described—one of low-boiling range, designated as "Cresol L B," and one of high-boiling range, "Cresol H B." The distillation data of these two cresols and of the kerosene employed in most of the work are given in Table 1.

One source of error in the Weiss-Hill method may lie in the removal of some kerosene along with the aqueous alkaline extract,

recognized as possible by Weiss, but apparently not regarded as quantitatively significant.

TABLE 1.—*Distillation data on cresols and kerosene*

[Temperatures as read, uncorrected, on a 14-inch thermometer, graduated from −30° to 400° C.]

Temperature ° C.	Percentage of total distilled—			Temperature ° C.	Percentage of total distilled—		
	Cresol L B.	Cresol H B.	Kerosene		Cresol L B.	Cresol H B.	Kerosene
	Per cent	*Per cent*	*Per cent*		*Per cent*	*Per cent*	*Per cent*
190	3.0			220		91.5	
200	58.0		13.5	225	98.0		
205		12.5		230			52.5
208		39.5		238		99.0	
210	94.0			250			75.5
212		67.5		340			97.0
215			31.5				

EXPERIMENT 2(a)

About 70 cubic centimeters of purified kerosene in a Weiss tar-acid funnel, type 2, were shaken with 25 cubic centimeters of 10 per cent NaOH solution and measured at 25° C. after complete removal of the aqueous layer. Then were added 25 cubic centimeters of m-cresol of "highest purity" and the solution was extracted three times with 10 per cent NaOH according to the details of the writer's "standard method," later given (p. 15). Final measurement at 25° C. showed a loss of 0.05 cubic centimeter in the volume of kerosene. A fourth extraction with 10 per cent NaOH solution effected no further perceptible diminution in volume.

EXPERIMENT 2(b)

Cresol H B was redistilled and 25 cubic centimeters were dissolved in 50 cubic centimeters C. P. benzene in a separatory funnel. The solution was first extracted with 25 cubic centimeters of 5 per cent H_2SO_4, then with 100 cubic centimeters of 10 per cent NaOH. The alkaline extract was diluted with 75 cubic centimeters of water and boiled to its original volume in a flask, the distillate being passed through a Wagner tube into 80 cubic centimeters of 10 per cent NaOH. The residue, thus freed from tar bases and oils, was shaken through kerosene in a type 2 tar-acid funnel, the kerosene having been measured at 25° C. after a preliminary shaking with 10 per cent NaOH. The distillate was shaken through the benzene solution left from the first alkaline extraction, boiled down to 80 cubic centimeters, and passed through the kerosene in the tar-acid funnel, after which the latter was finally extracted with 60 cubic centimeters more of the 10 per cent NaOH. The volume of kerosene at 25° C. became diminished by 0.10 cubic centimeter as the result of the operation.

It appears, then, that the operation of shaking out the phenols with 10 per cent sodium-hydroxide solution may be accompanied by a loss of between 0.05 and 0.10 cubic centimeters of the kerosene. The loss will naturally tend to increase with the boiling point of the phenols that are present, for with the increment of aliphatic side

chains the phenols should tend to resemble the fatty acids, the sodium salts of which possess marked power to dissolve and emulsify hydrocarbons.

A second possible error may lie in the assumption that admixture of kerosene and cresol is unattended by any change in volume.

EXPERIMENT 3(a)

Cresol L B was distilled and again reboiled in an open flask to insure elimination of water. Its specific gravity at 25° C. was 1.0330. It was then mixed with purified and dried kerosene of specific gravity 0.8063 in the proportion of 26.32 grams (≡25.58 cubic centimeters) cresol to 60.87 grams (≡75.79 cubic centimeters) kerosene. On a purely additive basis the 87.19 grams of the mixture should have possessed a total volume of 101.37 cubic centimeters. Its specific gravity was found to be 0.8625 at 25° C.; therefore its actual volume was 101.50 cubic centimeters, so that an expansion in volume on mixing at constant temperature occurred amounting to 0.13 cubic centimeter.

EXPERIMENT 3(b)

Cresol H B similarly treated showed an initial specific gravity of 1.0231. Mixed with kerosene of specific gravity 0.8088 in the proportion of 25.22 grams cresol (≡24.75 cubic centimeters) to 56.49 grams kerosene (≡70.12 cubic centimeters) the specific gravity of the mixture was 0.8638. The actual volume of the mixture at 25° C. was therefore 94.97 cubic centimeters, while the purely additive volume would be 94.87 cubic centimeters, or an expansion of 0.10 cubic centimeter was effected by mixing.

It appears, therefore, that the expansion in volume consequent upon the admixture of kerosene and cresol will cause the apparent volume of cresol to be between 0.10 and 0.13 cubic centimeter too great when about 25 cubic centimeters of cresol are present. Paraffin hydrocarbons are better solvents for higher boiling phenols than for the lower homologues; consequently the error should diminish as the boiling points of the phenols ascend.

A third, and probably the gravest and most erratic source of error in the Weiss-Hill method, lies in the incomplete elimination of water. Hill prescribes that—

> Where the sample to be tested contains water it should be removed by catching the first few cubic centimeters of distillate in a small separatory funnel containing a little saturated salt solution, separating the water and adding the oil to the rest of the distillate in the tar-acid funnel.

In the writer's experience traces of water are nearly always present in the first portions of distillate, and further traces are likely to arise from decomposition toward the end of the distillation. Sodium-chloride solution is not an effective dehydrating agent. In fact, solid salt will separate from a saturated solution of sodium chloride that is shaken with an anhydrous kerosene solution of cresol. Therefore this method for the removal of water merely means that a certain equilibrium proportion is left in the sample, and the procedure may actually introduce a higher proportion of water into a sample than was originally present, which water, of course, will be finally reckoned as "tar acid." The writer's remedy

is to collect the whole distillate in the tar-acid funnel and to dehydrate it by shaking with a sulphuric-acid solution of definite strength.

EXPERIMENT 4(a)

Twenty-five cubic centimeters of redistilled cresol L B were dissolved in about 70 cubic centimeters of purified kerosene in the tar-acid funnel. The solution was shaken with successive 50 cubic centimeter portions of sulphuric-acid solution of known specific gravity at $\frac{25°}{25°}$ C., and the corresponding changes in volume of the kerosene solution were noted, all measurements being made at 25° C. The first extraction removed tar bases. Subsequent extractions then involved only the distribution of tar acids and water between the two layers. Any one acid of specific gravity between 1.315 and 1.507, after the first extraction, effected a constant diminution of 0.30 cubic centimeter in the volume of the kerosene solution for each successive extraction, owing to loss of tar acids. All sulphuric acids of specific gravity between 1.451 and 1.507 were interchangeable; that is, no matter in what order these various acids were used for the extraction of a given kerosene solution, the decrease in volume was always 0.30 cubic centimeter per extraction, which means that all such acids were equally effective as dehydrating agents and that all must therefore have acted with practically 100 per cent efficiency. However, if treatment with any one of these acids were followed by a treatment with acid of specific gravity 1.398 or less, the decrease in volume was less than 0.30 cubic centimeter; and, conversely, if a treatment with acid of specific gravity 1.398 were followed by a treatment with acid of specific gravity 1.451 the decrease in volume was greater than 0.30 cubic centimeter, which means that acid of the lower gravity is an imperfect dehydrator. Acid of specific gravity 1.555 effected a constant decrease of nearly 0.40 cubic centimeter per treatment; that is, it extracted an inordinate proportion of tar acids as compared with acids of specific gravity 1.507 or less.

EXPERIMENT 4(b)

"Cresol H B," similarly treated, showed a constant decrease of 0.20 cubic centimeter for each extraction with 50 cubic centimeters of acid of specific gravity 1.505. Apparently, then, the distillates may be effectively dehydrated by extraction in the tar-acid funnel with a sufficient quantity of sulphuric acid of specific gravity 1.505 without danger of loss of tar acids except through simple solution. From specific-gravity tables it may be calculated that 100 cubic centimeters of an acid of 1.505 specific gravity will require 13 cubic centimeters of water to reduce it to a specific gravity of 1.451. Therefore the distillate in kerosene of 25 cubic centimeters of a cresol containing not over 13 per cent water may be completely dehydrated by shaking with 25 cubic centimeters of a sulphuric-acid solution of specific gravity 1.505 at a loss of between 0.10 and 0.15 cubic centimeters of the tar acids, the loss being less the lower the proportion of low-boiling homologues present.

It will be noted that the error due to solubility of tar acids in the sulphuric acid is of opposite sign from the errors due to expansion

in volume of cresol-kerosene mixtures and the solubility of kerosene in the alkaline aqueous extracts. Summation of the errors for an analysis performed as suggested will indicate that the result is likely to be in all cases a little too high, the error ranging from about 0.1 per cent for a low-boiling sample to nearly 0.4 per cent for a high-boiling sample.

Incidentally two additional sources of error are eliminated in the improved method: (1) Because in the Weiss-Hill method one measurement in the tar-acid funnel was made of oil plus tar acids in glass, whereas the second was made of oil over an aqueous film adherent to the glass; (2) because, as demonstrated by experiment, about two-thirds of any tar bases present, if not first extracted by acid, will pass into the alkaline extracts and will thus be reckoned as "tar acids."

The writer prefers the term "total phenols" for designating the sum total of the substances extracted by sodium hydroxide from a redistilled commercial cresol, and would restrict the term "tar acid" to such molecules as contain the carboxyl grouping. Organic acids in general readily react with aqueous solutions of sodium carbonate and even of bicarbonate; phenols, on the contrary, are inert and even tend to be salted out of aqueous solution by addition of carbonated alkali. The following group of experiments was designed to determine whether a separation between true acids and phenols might be effected by distillation over sodium carbonate or bicarbonate.

EXPERIMENT 5

The distillations and extractions of the samples were carried out according to the codified method later described (p. 15), except for the modifications noted in Table 2, wherein are also given the data obtained upon the effect of the presence of sodium carbonate or bicarbonate in the distillation flask.

TABLE 2.—*Effect of carbonated alkali upon the distillation of acids and phenols in experiment 5*

Nature of sample	Substances besides kerosene added before distillation	Apparent percentage total phenols			
		I	II	III	IV
		Per cent	*Per cent*	*Per cent*	*Per cent*
Cresol L B	None	95.6	96.0	----------	----------
Do	Solution Na_2CO_3 saturated at 25° C; (I) 2 c. c.; (II) 3 c. c.; (III) 1 c. c. plus 2 c. c. H_2O.	96.0	95.6	95.8	----------
Cresol H B	None	96.2	96.2	96.6	96.4
Do	Dry $NaHCO_3$; (I) 1 g.; (II) 2 g.	96.0	96.4	----------	----------
Do	Air-dried powdered Na_2CO_3, 2 g.	97.0	97.0	----------	----------
Do	2 c. c. coconut-oil fatty acids, (I) 2 g. $NaHCO_3$; (II) 2 g. airdried Na_2CO_3.	96.6	96.6	----------	----------

From experiment 5 it is apparent that under conditions ordinarily prevailing even sodium carbonate is inert toward phenols during distillation, but that both sodium carbonate and sodium bicarbonate can probably be trusted to hold back true acids of a nature likely to be present. In neither of the two samples of cresol did there appear

any evidence of the presence of true acids. Whether the addition of sodium bicarbonate need be made a matter of routine in the assay of commercial cresols for "total phenols" will have to be determined by some one with access to a wider variety of such products than are likely to come into the hands of the writer.

The foregoing study on the assay of commercial cresol points the way toward a practical method for the determination of total phenols in saponified cresol solutions. If sodium bicarbonate is added to a kerosene solution of the sample, then on distillation any original excess of sodium hydroxide which would otherwise tend to hold back phenols should be converted into innocuous sodium carbonate, while any original excess of fatty acid which might otherwise contaminate the distillate should be neutralized and held back.

EXPERIMENT 6

A saponified cresol solution was prepared from cresol H B as follows:

Soybean oil, 290 grams, was emulsified with a solution containing 42.3 grams NaOH in about twice its weight of water by stirring in a beaker. After several hours at room temperature saponification was completed by heating overnight on the steam bath with occasional stirring. The soap was then transferred to a flask together with 520 grams of cresol H B and sufficient water to bring the total weight of the mixture to 1,000 grams. Complete solution of the soap was effected in the stoppered flask at room temperature. The specific gravity of the completed "saponified cresol solution H B" was 1.0259 at $\frac{25^\circ}{25^\circ}$ C., so that the 1,000 grams occupied a volume of 979 cubic centimeters. The specific gravity of the cresol was 1.0225, and its purity had been shown by experiment 5 to be 96.3 volume per cent. Therefore there must have been 511 cubic centimeters of cresol H B, or 492 cubic centimeters actual phenols present, which makes the theoretical content of the saponified cresol solution 50.3 volume per cent of total phenols.

Portions of 40 cubic centimeters of saponified cresol solution H B were distilled in a 300 cubic centimeter flask provided with a thermometer with the addition of 75 cubic centimeters of kerosene, besides other additions later noted. The distillate in the tar-acid funnel was extracted twice with 20 cubic centimeter portions of sulphuric-acid solution, specific gravity 1.505, then three times with sodium-hydroxide solution, as in the assay of commercial cresol. To the decrease in volume of the kerosene layer was added a correction of 0.10 cubic centimeter to compensate for half the phenols extracted in the approximately 50 cubic centimeters of the acid layer, and the sum was divided by 0.4 to obtain the apparent volume per cent of phenols in the sample. The essential data are given in Table 3. The "maximum temperature" was that noted, without corrections, on a 16-inch thermometer graduated from −30° to 400° C.

TABLE 3.—*Data on determination of total phenols in 40 cubic-centimeter samples of saponified cresol solution H B in experiment 6*

Experiment number	Other additions besides kerosene	Maximum temperature	Apparent percentage of phenols
		°C	*Per cent*
a	1.6 c. c. of NaOH sol. (1 c. c.=0.516 g. NaOH)	280	44.8
b	Ditto, plus 2 g. $NaHCO_3$		48.8
c	Ditto, plus 4 g. $NaHCO_3$	277	50.1
d	4 g. $NaHCO_3$ only; no NaOH	280	50.0
e	do	260	48.0
f	Ditto, but using "topped" kerosene	281	50.1
g	4 g. $NaHCO_3$; 5 c. c. medicinal mineral oil	320	49.9

The data of Table 3 show that sodium bicarbonate is effective in neutralizing an excess of sodium hydroxide. The original saponified cresol solution was made to contain a slight theoretical excess of alkali (4.23 weight per cent against 4.03 theoretical), but the further addition of a 50 per cent excess of sodium hydroxide was taken care of by sodium bicarbonate when enough was present.

Experiment 6 (e) was purposely run to a low maximum temperature, which was evidently insufficient to expel all phenols. In experiment 6 (f) the kerosene had been previously "topped" to a temperature of 210° C. and the lower boiling fraction of about 24 per cent discarded, but no greater recovery of phenols was effected by the use of this material. Except for experiment 6(e) the maximum temperature noted was not a matter of choice, but was the maximum obtainable after which the thermometer began to drop owing to the high viscosity of the residue which cut down the rate of heat transfer and led to charring on the bottom of the flask. But evidently a nearly quantitative recovery of phenols is effected if the distillation is carried to this point.

In further work it seemed better to sacrifice a certain degree of precision by reducing the volume of the sample to 25 cubic centimeters, thus expediting the distillation, rendering the expulsion of phenols more certainly complete and eliminating the necessity for making a correction, always an undesirable feature in a practical method of analysis. Using two portions of 10 cubic centimeters each of sulphuric-acid solution for the acid extraction, the total volume of extract will be practically the same as that resulting in the assay of commercial cresol and will be automatically corrected for by the other errors of opposite sign inherent in the process, as in the assay of commercial cresol.

EXPERIMENT 7

Saponified cresol solution H B, 25.15 cubic centimeters, was distilled from a 200 cubic centimeter flask with 75 cubic centimeters kerosene and 2.5 grams sodium bicarbonate. Except for two experiments a thermometer was not used, for it was found that the maximum temperature was always above 280° C. and that it was surely passed if the distillation was continued until the distillate began to come over strongly yellow owing to incipient charring of the residue. The distillate was extracted in the tar-acid funnel with two portions of 10 cubic centimeters of sulphuric-acid solution of specific gravity 1.505. The second extraction removed not more than 0.20 cubic

centimeter, which indicated that water was thus completely eliminated. After measurement the acid-extracted kerosene solution of phenols was extracted twice with a 10 per cent solution of sodium hydroxide, using 80 cubic centimeters and 60 cubic centimeters and allowing draining periods of two hours and one hour, respectively.

The second extraction removed not more than 0.15 cubic centimeter, which indicated that a third extraction would be superfluous. The decrease in volume of kerosene was divided by 0.2515 to obtain the apparent volume percentage of phenols in the sample. Results obtained thus were as follows: I, 50.5; II, 50.7; III, 50.3; IV, 50.7; V, 49.9; VI, 49.9; VII, 49.9; VIII, 50.3. In Tests I to V, inclusive, commercial kerosene was used, inasmuch as the presence of sodium bicarbonate during distillation would seem to render purification unnecessary, but purified kerosene was used for the remainder. In Tests IV, V, VI, and VIII a very loose plug of well-teased glass wool was placed in the neck of the flask below the side tube to insure against the entrainment of soap. The extreme absolute error of any determination was thus ± 0.4 per cent. The separatory funnel is graduated only to 0.2 cubic centimeter and was read only to the nearest 0.05 cubic centimeter. Inasmuch as the aqueous liquids do not always leave a uniform film on the glass when drained from the funnel, it appears possible for a reading to be in error by ± 0.05 cubic centimeter. If the two readings on a determination are both subject to errors of 0.05 cubic centimeter, the total error of reading may be 0.10 cubic centimeter, corresponding to 0.4 per cent of the sample. Thus the observed error of the determinations is practically accounted for by the inherent error of the volumetric apparatus and the manner in which it is necessarily employed. A plug of glass wool appears superfluous, but it is probably best as a matter of principle to use only purified kerosene.

As a result of the foregoing work the writer recommends the following methods for the estimation of total phenols in commercial cresol and in saponified cresol solutions:

APPARATUS

Weiss tar-acid separatory funnel, type 2; 200 cubic centimeter hard-glass distilling flask; vertical water-cooled condenser; shield [2] for flask; standardized 25 cubic centimeter pipette; standardized 25 cubic centimeter cylinder.

REAGENTS

Sulphuric-acid solution, specific gravity 1.50–1.51 at 25° C.; sodium-hydroxide solution, substantially free from carbonate, specific gravity 1.10–1.11 at 25° C.; sodium bicarbonate in powder, free from lumps; kerosene, recently purified by being washed twice with one-tenth of its volume of sodium-hydroxide solution, then with water until neutral, and freed from water by settling and filtration.

PROCEDURE FOR CRESOL

The pipette is filled above the mark with the sample at 25° C., its stem wiped dry, the contents brought to the mark and then deliv-

[2] The most convenient shield is made from hard glass, and may be extemporized by removing the bottom from a hard-glass beaker of appropriate size. In other respects the distillation apparatus prescribed by Weiss is admirable.

ered into the distilling flask already containing 75 cubic centimeters of kerosene. The pipette is clamped vertically with its tip just below the surface of the kerosene and allowed to drain five minutes. The contents of the flask are then distilled to decomposition at a rate of not more than 2 drops per second from the condenser into the tar-acid separatory funnel. The distillate in the funnel is thoroughly shaken with 25 cubic centimeters of sulphuric acid solution, allowed to stand at least one-half hour, and then measured at 25° C. after the sulphuric acid has been thoroughly drained off. It is next extracted with three portions of sodium-hydroxide solution with a minimum period of rest between each agitation and separation as follows: (*a*) 100 cubic centimeters and three hours; (*b*) 80 cubic centimeters and two hours; (*c*) 60 cubic centimeters and one hour. After thorough draining it is again measured at 25° C. The difference between the two measurements multiplied by 4 represents the volume percentage of total phenols in the sample.

Precautions.—No loss of the upper layer on the removal of stoppers or from leaky stopcocks may be permitted. All insoluble matter at the interface should be left with the upper layer in each separation. If such insoluble matter is of significant volume at the end, about 5 cubic centimeters of sulphuric acid solution may be added, the tube well rotated in a vertical position between the palms of the hands, left at rest 15 minutes, and then drained for measurement. All drainages should be as complete as possible, and all readings should be made while the funnel is actually within a water bath of the prescribed temperature, as, for example, an ordinary liter cylinder.

PROCEDURE FOR SAPONIFIED CRESOL SOLUTIONS

The graduated cylinder is filled above the mark with the sample and a thermometer is used as a stirrer while the temperature is brought to 25° C. After withdrawal of the thermometer and the elimination of air bubbles all froth is removed with filter paper and the level of the liquid adjusted to the mark by aid of a pipette. The contents of the cylinder are completely transferred to the distilling flask by rinsing with 75 cubic centimeters of kerosene in successive portions; then 2.5 grams of sodium bicarbonate are added, or more if indicated necessary by the excess alkali determination, and the contents of the flask are mixed by swirling for one minute. The contents are then distilled at a rate of not more than 2 drops per second from the condenser into the tar-acid separatory funnel until the distillate comes over strongly yellow. The distillate in the funnel is shaken twice with 10 cubic-centimeter portions of sulphuric-acid solution, allowing at least one-half hour between each agitation and ensuing separation. After complete drainage of the second acid extract the distillate is measured at 25° C. and thereafter handled as prescribed in the procedure for cresol, except that the extraction with 100 cubic centimeters of sodium-hydroxide solution is omitted.

Precautions.—In addition to the precautions noted in the procedure for commercial cresol, special attention is necessary to avoid boiling over. The distillation is to be started with a low flame vertically under one side of the flask. As frothing lessens, the flame is moved toward the center, but it is then necessary to watch for a sudden, spontaneous increase in the violence of boiling that occurs

as soon as all water has passed off. The flame toward the end should be slightly luminous to mitigate local overheating of the flask. A 250-cubic centimeter flask may be used in lieu of the 200-cubic centimeter size. In dealing with opaque samples it will be necessary either to graduate a measuring cylinder to contain 25 cubic centimeters at the top of the meniscus, using for the purpose a transparent sample of a saponified cresol solution, or to determine the specific gravity of the sample and then to weigh out the equivalent of 25 cubic centimeters. Inasmuch as 1 cubic centimeter of water at 25° C. weighs 0.996 gram, the weight of 25 cubic centimeters of the sample will be 25 × specific gravity × 0.996 gram.

The possible seriousness of one weakness in the method may be determined only by subsequent extended practical experience. The quantitative recovery of the total phenols becomes more doubtful as their boiling points rise and as they are mixed with increasing proportions of soap. However, a limit is set to the proportion of soap by the necessity for passing the chill test and the solution-rate test, and a limit is set upon the proportion of inordinately high-boiling phenols by the necessity for passing the solubility-degree test. In view of these restrictions it is anticipated that no serious deficiency in the quantitative recovery of total phenols will be experienced in case of such samples as are, in other respects, fit for actual use.

The results are obtained in volume percentages but these are the same within the inherent limits of error of the method as the weight percentages, for the specific gravity of a saponified cresol solution differs but little from the specific gravity of the phenolic mixture used in its preparation. In experiment 6 the specific gravity of cresol H B was stated to be 1.0225, while that of saponified cresol solution H B was 1.0259. Cresol L B possessed a specific gravity of 1.034, while that of a saponified cresol solution prepared therefrom was found to be 1.030.

With respect to the assay of commercial cresol, it is possible that if sodium bicarbonate is not added and if the kerosene is first dried, a sufficiently accurate estimation of tar bases plus water may be made by measuring the volume of distillate before and after it is shaken with sulphuric-acid solution.

ESTIMATION OF BENZOPHENOL

The writer (*2*) has previously described a method for the estimation of benzophenol in the presence of its homologues; accordingly, the present discussion will be limited to the essentials necessary for the routine execution of the method.

REAGENTS

Dilute nitric acid is prepared by blowing air through C. P. concentrated nitric acid until colorless, then diluting 1 volume with 4 volumes of water. Millon's reagent is prepared from 2 cubic centimeters of mercury and 20 cubic centimeters of C. P. concentrated nitric acid in a 100 cubic centimeter Erlenmeyer flask placed under a hood and shaken as much as need be after the first violent reaction to effect subdivision of the mercury and maintain action. After about

10 minutes, when action has practically ceased even in presence of undissolved mercury, 35 cubic centimeters of water are added. If basic salt separates, dilute nitric acid is added to dissolve it. Sodium hydroxide, 10 per cent, is next added by drops with thorough mixing until the curdy precipitate following a single drop no longer redissolves but disperses to an evidently permanent turbidity. Then 5 cubic centimeters of dilute nitric acid are well mixed in. The solution is perfectly fit for use on the day following its preparation, but later deteriorates.

Standard benzophenol is prepared by dissolving a weighed amount of the pure substance, possessing a congealing point of not lower than 40° C., in water to make not less than a 1 per cent solution. From this stock solution is made a 0.025 per cent solution of phenol in distilled water, which constitutes the final standard and which should be prepared on the day of use. Dilute formaldehyde solution is prepared by diluting 2 cubic centimeters of the commercial 37 per cent solution to 100 cubic centimeters with distilled water.

APPARATUS

In addition to ordinary burettes, pipettes, and flasks are required matched Nessler cylinders, 50 cubic centimeters, tall form, and a supply of test tubes, about 180 by 20 millimeters, graduated at 25 cubic centimeters, for which a file scratch will serve, and provided with rubber stoppers; also a water bath for heating these tubes, which may be extemporized from a beaker containing a disk of wire gauze raised somewhat from the bottom.

PROCEDURE

In the case of a commercial cresol about 2.5 grams are weighed by difference into a 250 cubic centimeter volumetric flask, dissolved in 10 cubic centimeters of 10 per cent sodium-hydroxide solution and made to the mark with water. Shortly before the determination is to be executed 5 cubic centimeters of this solution are placed in a 200 cubic centimeter volumetric flask, and after dilution to about 50 cubic centimeters 1 drop of methyl-orange indicator is added and then dilute nitric acid until practical neutrality is reached, after which the solution is made to the mark and well mixed. In the case of a saponified cresol solution about 5 grams are taken, and are similarly diluted with water only. Of the diluted solution 5 cubic centimeters are placed in each of two of the graduated test tubes, and in each of two others are placed 5 cubic centimeters of the standard phenol solution. Then 5 cubic centimeters of the Millon reagent are flowed down the sides of each tube, mixed in, and the tubes are placed in a water bath already brought to boiling and maintained at boiling for exactly 30 minutes. They are then immediately and thoroughly cooled by immersion in a bath of cold water for at least 10 minutes, after which 5 cubic centimeters of the dilute nitric acid are added to each.

After brief mixing 3 cubic centimeters of the dilute formaldehyde are added to one of each pair of tubes; all are made to the 25 cubic centimeter mark with water, stoppered, and well shaken, then put aside to stand overnight. The next day the tubes to which formaldehyde had been added will have faded to a yellow, while the others

possess an orange or red tint. From each of the two benzophenol tubes 20 cubic centimeters will be pipetted into 100 cubic centimeter volumetric flasks, treated with 5 cubic centimeters of dilute nitric acid, made to the mark, and mixed. The red flask contains the "phenol standard"; the yellow the "phenol blank." These phenol solutions are transferred to burettes. Ten cubic centimeters of each sample solution are pipetted into a Nessler tube. The orange constitutes the "unknown" and the yellow the "sample blank," and each Nessler tube must be distinctly marked thus to avoid confusion later. Now, into the "sample blank" is run a measured amount of phenol standard from its burette, and the same volume of phenol blank is run into the "unknown"; both tubes are well agitated, aided by the insertion of rubber stoppers, if necessary, and the colors compared. When the tubes have been brought directly to a match each 1 cubic centimeter of the phenol standard employed is equivalent to 2 per cent of benzophenol if the original sample was 2.5 grams of a commercial cresol, or to 1 per cent if it was 5 grams of a saponified cresol solution.

Precautions.—A pair of phenol tubes affords sufficient final solutions for assaying several unknowns, but all the latter must have accompanied the phenol solutions throughout the entire process with identical reagents and treatment. If the end point has been inadvertently overrun it is possible to work back to it; but, since mistakes are easy to make in this procedure, it is better to repeat the comparison on fresh portions from the original tubes. Too much delay in matching the tubes must be avoided once the titration has been started, else the excess of formaldehyde yet present in the blanks may have time to affect the intensity of the red after admixture. Millon solution is too dangerously poisonous and corrosive to justify the risk of using an ordinary pipette with suction by the unprotected mouth for its transference.

It may be noted that the quantity of the phenols entering a single test, about 1.25 milligrams, is much less than the 4 milligrams employed in the original paper. (*2*) It was then shown that the method gave distinctly low results, supposedly owing to the effect of formaldehyde. Later investigations have indicated the low results to be, in fact, primarily due to the adsorption of the red color by the yellow precipitates produced from the higher homologues of phenol. As the concentration of the total phenols in the sample is reduced, these precipitates become of less significance and the results for benzophenol approach the theoretical, as will be evident from experiment 8 correlative with experiments described in the paper referred to (*2*).

EXPERIMENT 8

A solution of cresol was prepared by blending equal volumes of 0=, m=, and p= cresol of "highest purity," and dissolving in water. Portions of this solution were mixed with an aqueous solution of pure benzophenol in proportions to afford mixtures of known concentration in total phenols and in benzophenol, and these mixtures were assayed. The concentration of benzophenol in the standard solution was in each assay equal to the concentration of the total phenols in the sample. The work and its results are sufficiently explained by the data contained in Table 4.

TABLE 4.—*Estimation of benzophenol in the known mixtures described in experiment 8*

Quantity of total phenols in sample	Ratios of benzophenol to total phenols				
	0/100	2.5/100	5/100	10/100	20/100
	Per cent found	*Per cent found*	*Per cent found*	*Per cent found*	*Per cent found*
4 milligrams [1]		[1] 1.9	[1] 4.0	[1] 8.5	[1] 18.6
2.5 milligrams	0.1	2.2	4.4	9.5	20.0
1.25 milligrams		2.4	4.8		

[1] From paper referred to (2).

FRACTIONAL DISTILLATION OF THE TOTAL PHENOLS

The isolation of the total phenols from a saponified cresol solution in a quantity and condition suitable for a complete fractional distillation appears to be too tedious an undertaking to be practical. But the determination of benzophenol removes any necessity for fractional distillation over the lower range of temperatures, so that only a single temperature reading in the higher range is needed for the purpose of detecting the presence of significant proportions of high-boiling phenols.

If the sample is a saponified cresol solution, the alkaline extracts from the estimation of total phenols are saved and serially shaken through 20 cubic centimeters of petroleum ether to insure the removal of traces of kerosene, etc. They are next united in a 250-cubic centimeter Erlenmeyer flask containing a scrap of Congo-red test paper and acidified with concentrated hydrochloric acid. The contents of the flask, when cold, together with 50 cubic centimeters of ethyl ether used to rinse it, are transferred to a separatory funnel, shaken, and separated after the ether solution has become perfectly clear. After the aqueous layer has been completely drained from the funnel the ether solution is transferred to a 150-cubic centimeter flask and most of the ether is evaporated on the steam bath. A 25-cubic centimeter distilling flask of hard glass, with a neck measuring about 6 centimeters in length, and with a side tube at the middle of the neck, is weighed when clean, dry, and containing a few grains of powdered zinc. The phenolic residue is rinsed into the flask with a little ether or benzene; then the flask is set inside a bottomless hard-glass beaker as a shield, which rests on an asbestos board provided with an evenly circular perforation 2 centimeters in diameter, snugly covered by the bottom of the flask. The thermometer must be of the short-stemmed type and should be fixed with its bulb midway between the bottom of the neck and the side tube of the flask. The flask should be supported in an upright position and connected to a condenser of any convenient type.

Distillation is conducted in the customary manner until the thermometer indicates the chosen temperature, making allowance for all corrections, at which point the flame is quickly taken away. After the flask has cooled the corks are removed, the inside of the neck above the side tube and the side tube itself are freed from condensate by twists of filter paper or cotton; then the flask and contents are

weighed and the weight of undistilled residue is multiplied by 4 to obtain the percentage of high-boiling phenols in the sample.

Samples of commercial cresol should probably be subjected to direct distillation of 25 grams in a 50-cubic centimeter flask, though obviously it is possible to recover the phenols from the alkaline extract from the estimation of total phenols, as in the case of saponified cresol solutions.

TENTATIVE STANDARDS AND RESULTS OF THE EXAMINATION OF SOME COMMERCIAL SAMPLES

For purposes of control it is necessary to set entirely definite standards for performance and composition. Such standards must be rigorous enough to insure adequate quality but at the same time liberal enough to assure a sufficient supply of the commercial product at a reasonable price. In this section the writer accordingly offers in a wholly tentative way provisional standards formulated on the basis of his own experience, together with the results of the examination of a number of commercial samples. The latter have been selected to cover the widest range of composition thus far met and include some samples of material supplied as "Liquor Cresolis Compositus, U. S. P."

In the chill test the tubes were packed in sufficient cracked ice to insure a temperature of 0° C. throughout the period of exposure, which was set at three hours. A shorter period is not always sufficient to allow a tendency toward separation or gelatinization to become plainly manifest. The rate and degree of solubility were determined in water at 25° C., and two minutes was tentatively adopted as the maximum period which should be necessary for complete solution.

The Bureau of Animal Industry (*6*) at present requires a soap content equivalent to not less than 28 per cent linseed oil or soybean oil. The saponification values of these oils range from 187 to 200, so that if completely saponified 28 per cent of glyceride will be equivalent to between 3.73 and 3.99 per cent of combined sodium hydroxide. It is important that saponification should be practically complete; therefore it appears fitting to require that the alkali combined as soap shall be equivalent to not less than 3.6 per cent sodium hydroxide. Perhaps the excess alkali may be justifiably limited to not more than 0.5 per cent, expressed as sodium hydroxide. A minimum content of 50 per cent total phenols is already required by B. A. I. Order 273. Perhaps the maximum limit might be placed at 53 per cent.

The temperature at which to stop distillation in the determination of high-boiling phenols was tentatively fixed at 207° C., corrected, midway between the boiling points of meta- and paracresols (202° C.) and the lowest-boiling xylenol (211.5° C.). In addition, a few results are given at 210° C. and 215° C., corrected. The thermometer was standardized by distilling a sample of paracresol of assured high purity in the apparatus used for the determination of high-boiling phenols and reading the temperature at the middle of the distillation. All temperatures were reduced to 760 millimeters barometric pressure at 0° C. by first reducing the observed barometric reading to 0° C. (8°≡1 millimeter) and then correcting for the difference between the latter and 760 millimeters (1 millimeter≡.037° C.).

TABLE 5.—*Results of examination of commercial samples*

Sample number	Chill test; result	Solution—rate test; time	Solution—degree test; result	Total phenols	High-boiling phenols			Benzophenol	Alkali as soap; per cent as NaOH	Excess alkali; per cent as NaOH
					Above 207° C.	Above 210° C.	Above 215° C.			
		Min. Sec.		*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
1	Passed		Failed	53.2	51.3		12.8		4.15	0.10
2	do		do	50.0	47.1		14.1		3.88	.33
3	do		do	48.2	36.5			2.8	4.15	.36
4	do		do	45.0		21.4		1.4	4.48	.14
5	do	1 55	Passed	51.8	27.9		8.6	4.1	3.87	.95
6	do	2 10	do	51.4	25.7			2.0	4.03	.06
7	do	2 10	do	44.6	23.6		9.8	4.5	4.15	.67
8	Jelled	2 --	Failed	52.0	18.8	8.5		1.2	4.36	.73
9		1 40	Passed	51.0	18.8		3.6	2.5	3.48	.70
10	Passed	1 40	do	50.6	8.2		2.4	3.3	4.24	.18
11		1 35	do	51.2	7.8			4.6	4.16	.16
12	Passed	1 30	do	50.8	7.4			3.6	4.03	[2]—.08
13		1 20	do	50.6	6.8	3.5		6.2	3.99	.27
14	Passed	1 25	do	49.0	6.0		2.6	8.3	3.98	1.12
15		[1]	do	50.0	4.9			14.6	4.12	.31
16	Passed	1 25	do	46.2	3.8			6.6		
17		1 20	do	52.4	2.8			3.9		
18	Passed	1 30	do	55.8	2.0			.5		

[1] The sample diffused immediately upon contact with water.
[2] That is, the sample contained *free acid* equivalent to 0.08 per cent NaOH

The samples composing Table 5 are arranged in the descending order of their percentage contents of high-boiling phenols, and the important influence of this constituent will be readily perceived. It may be judged that a content of 30 per cent of phenols boiling above 207° C. marks the maximum limit in a saponified cresol solution that is likely to be satisfactory in rate and degree of solubility; even then products near the limit may require special formulas, such as the use of potassium hydroxide instead of sodium hydroxide, in order to secure satisfactorily rapid solution. The failure of sample No. 8 to afford a perfect solution must probably be attributed to the presence of an inordinate proportion of oily matter of some description. The admissible content of benzophenol may perhaps be limited to 7.5 per cent, equivalent to about 15 per cent in the original commercial cresol.

The requirements and specifications herein suggested will be most easily met by a manufacturer who employs a low-boiling commercial cresol, provided, of course, that he guards against an excessive proportion of benzophenol. The higher the boiling range of the commercial cresol the more likely is the finished product to afford globules upon dilution with water. To correct this fault it may be necessary to increase the percentage of soap. But with an increased proportion of soap the product may become too slowly soluble and too easily separated by chilling. To avoid these troubles in turn it will be necessary to use only the softer and more soluble soaps; that is, those which contain predominantly such fatty acids as are either of low molecular weight or highly "unsaturated" with respect to their hydrogen content. As a last resort it may be necessary to use potassium hydroxide instead of sodium hydroxide in making the soap. The formation of globules is also naturally promoted by hydrocarbons in the commercial cresol and by unsaponified oil in the soap.

SUMMARY

The aim of this work has been to develop convenient but effective methods for the control of saponified cresol solutions, particularly the proprietary brands employed in official disinfection under supervision of the Bureau of Animal Industry. (*6*) The functions which such preparations must perform in the field have been reviewed and a set of specifications drawn to cover the evident requirements. Tentative standards for performance and composition are proposed.

The chemical and physical tests described are limited to those necessary for determining whether samples comply with the specifications and standards formulated. These tests are new in some respects, particularly in details of technic whereby methods of recognized value in other fields have been made applicable to saponified cresol solutions.

A table of results on a number of commercial samples indicates the range of composition and properties which prevails at present.

It must be expressly noted that nothing in this bulletin operates to modify in any respect the specifications and requirements which have been issued or which may be issued by regulatory offices of the Bureau of Animal Industry governing products permitted for use in official disinfection.

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